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(54) **High-aluminium-containing ferritic stainless steel.**

(57) A ferritic stainless steel, consisting of, in weight percent: less than 0.03 % carbon, less than 1 % silicon, less than 1 % manganese, less than 0.04 % phosphorus, less than 0.03 % sulphur, from 15 % to 25 % chromium, less than 0.03 % nitrogen, from 3 % to 6% aluminium, from 0.1 % to 4 % molybdenum, from 0.01 % to 0.15 % yttrium and/or rare-earth elements, the balance being iron. Optionally, from 0.05 to 1% of one or more of the elements niobium, vanadium and titanium may be added.

The steel of the invention exhibits a high oxidation resistance at high temperatures, and is suitable for catalytic convertors for exhaust systems and also for heating devices.

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The present invention relates to a high-aluminium-containing ferritic stainless steel which can have improved high-temperature oxidation resistance, useful in high-temperature applications such as in catalysts for emission control system for motor vehicles, a heating device, and others.

High-aluminium ferritic stainless steels have a high oxidation resistance at high temperature so. They are extensively used for materials in heating devices such as a stove pipe, and electric heater elements.

Ceramics have heretofore been used as a catalyst carrier of a catalytic converter provided in an emission control system for motor vehicles, and ferritic stainless steel is now beginning to be used instead. One of the defects of the ceramic is that the ceramic is vulnerable to thermal shock. Another is that the ceramic has a high heat capacity. Consequently, when the ceramic is used for a catalyst carrier, a long time is required to be heated to a catalyst reacting temperature. A metallic carrier made of high-aluminum ferritic stainless steel does not have such defects as the ceramic.

The stainless steel is formed into a sheet of foil having a thickness of about 50μm to be used as a catalyst carrier for catalytic converters. Since abnormal oxidation is liable to occur on the foil and the converter is used in an atmosphere of exhaust gases representing severe oxidization conditions, the foil must have extremely resistive characteristics against high-temperature oxidation. To meet the requirements, a high-aluminium-containing ferritic stainless steel including 20Cr-5Al as a base, rare-earth elements and yttrium is used. However, such a stainless steel does not have sufficient high-temperature oxidation resistance, so that an extended use of the steel causes abnormal oxidation.

In addition, from the point of global warming and public nuisance, stricter limits have been imposed on emission control. To comply with the standards, it is necessary to quickly heat the catalyst to the catalyst reacting temperature after the start of the engine. To this end, the temperature of exhaust gas is elevated, or the converter is positioned directly under an exhaust manifold. On the other hand, the power of the engine tends to be increased in recent years, which increases the temperature of the exhaust. These conditions enhance oxidation and corrosion of the catalyst carrier. Therefore, it is desirable to provide a high-aluminium-containing ferritic stainless steel having improved high-temperature oxidation resistance.

In order to improve the resistance of the high-aluminium-containing ferritic stainless steel against high-temperature oxidation, contents of chrominum, aluminium rare earth elements and yttrium are increased, which is disclosed in Japanese Patent Application Laid-Open 63-45351. However, slabs and hot-rolled plates made of such a stainless steel are poor in toughness and hence, in productivity. More particularly, increase in chromium and aluminium contents not only increases cost of the component material, but also decreases productivity due to poor toughness. As a consequence the yield of the stainless steel decreases, thereby increasing manufacturing cost, or the production becomes altogether impossible. Alternatively, a rare-earth element and/or yttrium are added to promote high-temperature oxidation resistance. However, excessive quantity of these elements rather decreases the high-temperature oxidation resistance, and causes deterioration in toughness.

In addition, the ferritic stainless steel foil of the catalytic converter is subjected to heat cycles where heating and cooling are repeated, thereby causing deformation of the foil. Thus, the catalyst carrier should have high heat resistance.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a ferritic stainless steel where the high-temperature oxidation resistance is improved without increasing contents of some components, thereby improving production

According to the present invention, the material of a high-aluminium ferritic stainless steel having high-temperature oxidation resistance contains by weight of under 0.03 % carbon, under 1 % silicon, under 1 % manganese under 0.04 % phosphorus, under 0.003 % sulphur, from 15 % to 25 % chromium, under 0.03 % nitrogen, from 3 % to 6 % aluminium from 0.1 % to 4 % molybdenum, and from 0.01 % to 0.15 % in total of one or more rare-earth elements and yttrium.

By weight of 0.05 % to 1 % in total of one or more of niobium, vanadium and titanium is preferably included in the material.

When molybdenum and small quantities of rare earth elements and yttrium are included in the high-aluminium containing ferritic stainless steel, high-temperature oxidation resistance and heat resistance are improved so as to be applicable to a catalyst carrier in an emission control system for motor vehicles, heating devices and electric heater elements.

In order that the invention may be illustrated and readily carried into effect, preferred embodiments thereof are now presented by way of example only and described with reference to the accompanying Figure.

The figure is a graph showing a relationship between a quantity of molybdenum and a time elapsed before the occurrence of abnormal oxidation.

Content of each component and reason for numerical limitation of the content are described hereinafter.

(Carbon C)

Excessive content of carbon in high-aluminium-containing ferritic stainless steel induces abnormal oxidation and decreases toughness of the slabs and hot foils. The decrease of the toughness causes reduction of productivity of the steel. Therefore, the maximum content of the carbon is limited to 0.03 % by weight in the present invention.

(Silicon Si)

Silicon increases the hardness of the ferritic stainless steel and hence decreases the toughness thereof so that the content thereof is under 1 % by weight.

(Manganese Mn)

Manganese, although effective in enhancing hot workability, decreases the high-temperature oxidation resistance. Thus the content of manganese is limited to under 1 % by weight.

(Phosphorus P)

Since phosphorus affects the high-temperature oxidation resistance, it is preferable to limit the content thereof as small as possible. In addition, phophrorus also reduces toughness of the hot-rolled plate. Thus, the content of phosphorus is set under 0.04 % by weight.

(Sulphur S)

Sulphur combines with rare-earth elements and yttrium to form a nonmetallic inclusion which affects the surface quality of stainless steel. Sulphur may further decrease the effective quantities of the rare earth elements and yttrium which are effective in improving oxidation resistance. The significance of theses defects intensifies if over 0.003 % by weight of sulphur is included. Hence under 0.003 % by weight, preferably under 0.002 % by weight of sulphur is included.

(Chromium Cr)

Chromium is a basic element for improving high-temperature oxidation resistance. Content in excess of 15 % by weight of chronium is necessary for effectuating the improvement. However, if chromium in excess of 25 % by weight is included, toughness of slab and hot foil deteriorates, thereby reducing productivity. Hence the chromium content is between 15 % to 25 % by weight.

(Nitrogen N)

Nitrogen, when reacted with aluminium forms aluminium nitride (AlN) which induces abnormal oxidation. As the content of nitrogen is increased, toughness of the stainless steel deteriorates. Hence the content of nitrogen is under 0.03 % by weight.

(Aluminium Al)

Aluminium as well as chromium, is a significant element in maintaining the high-temperature oxidation resistance of the stainless steel. More particularly, an aluminium oxide film (Al_2O_3) is formed on the surface of the stainless steel by adding aluminum. The aluminium oxide film promotes the resistance. In order to restrain abnormal oxidation, which is liable to occur on foil having a thickness under 100µm, aluminium contents over 3 % by weight should be included so as to form sufficient aluminium oxide film on the surface. However, if the content of aluminium exceeds 6 % by weight, the toughness of slab and hot foil deteriorates. Thus, the aluminium content is from 3 % to 6 % by weight.

(Molybdenum Mo)

Since molybdenum produces a highly volatile oxide, it has been thought as an element which aggravates the high-temperature resistance. However, the inventors of the present invention have found on the contrary that molybdenum improves the high-temperature resistance, as well as heat resistance of the steel. The effect becomes apparent when the molybdenum content is over 0.1 % by weight as shown in the graph of the figure. However, if the content exceeds 4 % by weight, toughness of the stainless steel decreases, thereby affecting productivity. Hence the molybdenum content is between 0.1 % and 4 % by weight.

(Rare Earth Elements and Yttrium)

Rare earth elements and yttrium are important elements in improving high-temperature oxidation resistance in iron-chromium-aluminium stainless steels. Rare earth elements such as lanthanum and cerium, and yttrium are effective in stabilizing aluminium oxide (Al_2O_3) film formed on the surface of the stainless steel, and hence in restraining abnormal oxidation which is liable to occur on the stainless steel foil. In addition, the oxide film on the steel base is stabilized by the rare earth elements and yttrium. These effects become significant if over 0.01 % by weight of at least one of: rare earth elements and yttrium are included in total. If the contents thereof exceed 0.15 % by weight, hot workability and toughness decreases. Moreover, nonmetallic inclusions which induce the abnormal oxidation is easily formed. As a result, the high-temperature oxidation resistance is deteriorated contrary to the intention. Therefore, one or more of the rare earth elements and yttrium are included in the range of 0.01 % to 0.15 % by weight in total.

(Niobium, Vanadium and Titanium Nb, V, Ti)

Adequate quantities of niobium, vanadium and titanium may be included in the stainless steel to be bonded with carbon and nitrogen therein so that the toughness is significantly improved. Niobium, vanadium and titanium are also effective in improving heat resistance of the metallic carrier of a catalyst converter which tends to be deformed through repeated heating and cooling in heat cycles. In order to prevent the deformation, it is preferred to include one or more of niobium, vanadium and titanium in content over 0.05 % by weight in total. However, if the content exceeds 1 % by weight, the hardness of the stainless steel becomes too high. Thus, 0.05 % to 1 % of niobium, vanadium and titanium is preferably included.

Examples of the present invention are described hereinafter.

High-temperature oxidation resistance of the high-aluminium-containing ferritic stainless steel is imparted by an aluminium oxide film layer formed on the surface thereof. In order to stabilize the aluminium oxide film, it is effective to increase the content of chromium. However, in an ordinary iron-chromium-aluminium stainless steel, the oxide film is not sufficiently adhered, so that the film may flake off during a cooling process of the steel, causing abnormal oxidation.

Table 1 shows results of oxidation tests performed on various ferritic stainless steel to examine influence of the components on time at which abnormal oxidation occurs. Each of the ferritic stainless steel test pieces has a thickness of 50 µm. The test pieces were inserted in a heating furnance disposed in the atmosphere and maintained at a temperature of 1150°C. The test pieces were taken out of the furnance sometimes and observed by the naked eye for inspecting abnormal oxide in the form of projection other than normally existing thin and uniform oxide film. The abnormal oxidation occurrence time shown in the table indicates a length of time until the abnormal oxide occurs. As apparent from the Table 1, the stainless steel containing rare-earth elements (REM) or yttrium has far longer abnormal oxidation occurrence time than 20Cr-5Al steel (test piece A), thus showing improved high-temperature oxidation resistance.

TABLE 1

TEST PIECE		A	B	C
COMPONENT AND CONTENT (WEIGHT PERCENT)	C	0.014	0.023	0.012
	Si	0.34	0.32	0.32
	Mn	0.32	0.35	0.31
	P	0.025	0.023	0.025
	S	0.0022	0.0019	0.0022
	Cr	20.05	20.02	20.09
	N	0.014	0.014	0.012
	Al	4.87	5.01	5.02
	REM	–	0.06	–
	Y	–	–	0.05
ABNORMAL OXIDATION OCCURRENCE TIME		45	210	250

Heretofore steel having an oxidation resistance withstanding 100 hours at 1150°C was used for a catalyst converter carrier. However, the environment in which the present ferritic stainless steel is used has become much more severe than before as hereinbefore described. Therefore, it is presumed that the catalyst carrier has an abnormal oxidation occurrence time more than 300 hours. Hence the oxidation resistance of the stainless steels shown in Table 1 is not sufficient.

Accordingly, as shown in Table 2, the quantities of aluminium yttrium and rare-earth elements which are effective in improving high-temperature oxidation resistance were increased. The steels were melted in a 30kg vacuum melting furnance and cast into a steel ingot. However, when the ingot was hot forged, steel was cracked. Namely, the addition of excessive quantities of aluminium yttrium and rare-earth elements proved to be an inadequate solution from the point of productivity.

TABLE 2

TEST PIECE		P	Q	R
COMPONENT AND CONTENT (WEIGHT PERCENT)	C	0.012	0.011	0.014
	Si	0.33	0.30	0.30
	Mn	0.37	0.39	0.39
	P	0.025	0.025	0.025
	S	0.0020	0.0019	0.0020
	Cr	20.01	20.04	20.09
	N	0.012	0.011	0.014
	Al	5.08	6.25	5.07
	REM	0.15	0.09	–
	Y	0.03	–	0.09*
RESULTS OF FORGING		CRACKS FOUND	CRACKS FOUND	CRACKS FOUND

The inventors of the present invention have conducted various studies and experiments to obtain a steel having an improved high-temperature oxidation resistance without increasing the contents of aluminium yttrium and rare earth elements. Namely, influence of molybdenum on high-temperature oxidation resistance was investigated under the temperature of 1150°C using ferritic stainless steel foils having a thickness of 50 µm. The stainless steels were also wrought into honeycomb carriers for a catalytic converter having a diameter of 50mm, length of 100mm and a height of 1.5mm. One-hundred cooling and heating cycles in which the test pieces were subjected to temperatures of 900°C and 200°C for thirty minutes, respectively, were performed to examine the deformations thereof.

TABLE 3

	TEST PIECE	D	E	F	G	H	I
COMPONENT AND CONTENT (WEIGHT PERCENT)	C	0.026	0.021	0.023	0.014	0.015	0.013
	Si	0.31	0.31	0.32	0.31	0.34	0.30
	Mn	0.27	0.24	0.25	0.29	0.25	0.30
	P	0.024	0.024	0.024	0.025	0.024	0.025
	S	0.0019	0.0018	0.0021	0.0023	0.0021	0.0020
	Cr	20.04	20.08	20.03	20.09	20.10	20.07
	N	0.013	0.011	0.013	0.012	0.010	0.012
	Al	5.09	5.10	5.11	5.10	5.13	5.09
	REM	0.09	0.09	0.09	0.08	0.09	0.08
	Mo	-	0.19	0.51	1.13	2.35	3.87
ABNORMAL OXIDETION OCCURRENCE TIME		240	310	330	500	610	740
DEFORMATION		FOUND	NOT FOUND	NOT FOUND	NOT FOUND	NOT FOUND	NOT FOUND

As shown in Table 3, the abnormal oxidation occurrence time in each of the test pieces which includes molybdenum was extremely extended, that is, the high-temperature oxidation resistance was remarkably improved. The results show that the molybdenum acts to enhance the oxidation resistance characteristic of the aluminium oxide (Al_2O_3) formed on the iron-chromium-aluminium stainless steel including rare-earth elements and yttrium. The reason of the improvement in the high-temperature oxide resistance is not quite clear but without being bound by theoretical considerations, we postulate that molybdenum dissolves in the aluminium oxide film, thereby covering defects of the oxide film, preventing the oxygen from entering. Additionally, deformation of the steel did not occur through the cooling and heating cycles so that it can be said that the heat resistance is also improved.

Thus, the high-aluminium-containing ferritic stainless steel of the present invention including molybdenum has better resistance against high-temperature oxidation and has a high-temperature strength

compared to a conventional iron-chromium-aluminium stainless steel with or without rare earth elements and yttrium.

The examples of the ferritic stainless according to the present invention are described hereinafter.

Each of components of the ferritic stainless steel listed in Table 4 was vacuum-melted, forged, cut and hot-rolled, and thereafter repeatedly annealed and cold-rolled to form a piece of foil having a thickness of 50 µm. The test piece was heated for the oxidation test at 1150°C until oxidation was observed. The stainless steel foil was further wrought into a honeycomb carrier for a catalytic converter. Five-hundred cooling and heating cycles each of which comprising keeping the test piece in an exhaust gas atmosphere at a temperature of 200°C for five minutes and thereafter at a temperature of 900°C for thirty minutes. The abnormal oxidation occurrence time of each specimen and the deformation of the honeycomb made from the specimen were examined as shown in Table 4.

TABLE 4

CONTINUES...

	Specimen No.	Component and Content (Weight Percent)							
		C	Si	Mn	P	S	Cr	Al	N
Present Invention	1	0.014	0.35	0.24	0.025	0.0021	20.09	5.12	0.012
	2	0.017	0.31	0.22	0.024	0.0018	20.15	5.09	0.011
	3	0.019	0.32	0.24	0.024	0.0019	20.04	5.11	0.010
	4	0.012	0.33	0.22	0.025	0.0020	20.06	4.95	0.017
	5	0.011	0.30	0.33	0.025	0.0015	16.03	5.73	0.013
	6	0.014	0.34	0.26	0.025	0.0022	23.05	3.26	0.013
	7	0.013	0.33	0.53	0.025	0.0020	20.27	5.13	0.014
	8	0.015	0.33	0.27	0.025	0.0022	18.33	6.04	0.008
	9	0.011	0.31	0.26	0.025	0.0021	20.13	5.05	0.012
	10	0.015	0.35	0.22	0.025	0.0019	18.15	4.11	0.015
Comparative Example	11	0.014	0.34	0.24	0.025	0.0021	20.12	6.02	0.012
	12	0.017	0.31	0.31	0.024	0.0021	20.22	6.19	0.014
	13	0.019	0.30	0.33	0.024	0.0023	20.24	5.01	0.016
	14	0.012	0.34	0.32	0.025	0.0020	20.11	4.99	0.017
	15	0.011	0.30	0.31	0.025	0.0015	16.11	5.68	0.013
	16	0.014	0.33	0.31	0.025	0.0019	22.98	3.35	0.012
	17	0.013	0.32	0.33	0.025	0.0023	20.18	5.03	0.021
	18	0.016	0.32	0.27	0.025	0.0021	18.19	6.14	0.011
	19	0.013	0.32	0.36	0.025	0.0021	20.93	5.09	0.010
	20	0.014	0.33	0.22	0.025	0.0023	18.23	4.13	0.010

TABLE 4

... CONTINUED FROM PREVIOUS PAGE

Component and Content (Weight Percent)					Abnormal Oxidation Occurrence Time (Hours)	Deformation	Specimen No
La	Ce	Y	Mo	Remainder			
0.03	0.02	–	0.51		320	Not Found	1
0.05	–	–	1.08		490	Not Found	2
–	–	0.07	2.09		590	Not Found	3
0.02	0.01	0.02	3.12		700	Not Found	4
0.06	–	–	2.01		420	Not Found	5
0.03	0.02	0.02	2.14		380	Not Found	6
0.03	–	0.02	2.12	Nb: 0.28 V : 0.11	410	Not Found	7
0.08	–	–	1.97	Ti: 0.22	420	Not Found	8
0.05	–	–	2.10	V : 0.07	320	Not Found	9
–	0.06	–	3.94	Ti: 0.31	320	Not Found	10
0.03	0.03	–	–		240	Found	11
0.05	–	–	–		250	Found	12
–	–	0.05	–		240	Found	13
0.03	0.01	0.02	–		190	Found	14
0.06	–	–	–		170	Found	15
0.03	0.02	0.02	–		190	Found	16
0.03	–	0.02	–	Nb: 0.25 V : 0.13	120	Some Found	17
0.07	–	–	–	Ti: 0.18	130	Some Found	18
0.05	–	–	–	V : 0.09	110	Some Found	19
–	0.06	–	–	Ti: 0.29	90	Some Found	20

As is understood from the Table 4, each of the specimens according to the present invention has excellent high-temperature oxidation resistance. Namely, oxidation did not appear for over 300 hours in the examples of the present invention, whereas the comparative stainless steels without molybdenum assumed abnormal oxidation within 300 hours. Thus, the stainless steel of the present invention satisfies the desired characteristics for a catalyst carrier of an automotive catalytic converter. Furthermore, no deformation occurred in the test piece of the present invention. To the contrary, deformation was observed in the comparative example, that is, in specimens Nos. 11 to 16. Each of the specimens Nos. 17 to 20 having niobium, vandium and titanium has a slight effect to prevent the deformation, but is not sufficient.

The components of the stainless steels shown in Table 5 were melted in 30kg vacuum melting furnance, forged and annealed. In accordance with the testing method defined in JIS (Japanese Industrial Standard) G057, test pieces, each having a length of 50mm at a parallel portion and a diameter of 10mm were cut out from the ferritic stainless steel. The tension test for examining 0.2% proof stress and tensile strength was conducted at 800 °C.

TABLE 5

		PRESENT INVENTION		COMPARATIVE EXAMPLE	
SPECIMEN No.		21	22	23	24
COMPONENT AND CONTENT (WEIGHT PERCENT)	C	0.015	0.013	0.013	0.014
	Si	0.31	0.31	0.33	0.32
	Mn	0.23	0.25	0.21	0.18
	P	0.025	0.024	0.025	0.024
	S	0.0021	0.0019	0.0019	0.0022
	Cr	20.06	20.05	20.08	20.03
	N	0.015	0.014	0.015	0.013
	Al	5.11	5.08	5.10	5.12
	La	0.10	–	–	0.09
	Y	–	0.09	–	–
	Mo	2.02	2.12	–	–
0.2% PROOF STRESS (kg/mm^2)		6.8	5.1	4.2	4.4
TENSILE STRENGTH (kg/mm^2)		9.9	7.2	6.0	6.4

As shown in Table 5, test pieces of specimens Nos. 21 and 22 of the present invention had both higher proof stress and tensile strength than those of comparative examples, specimens Nos. 23 and 24, thus, showing improved strength at high temperature.

The test results show that the stainless steel in accordance with the present invention has excellent high-temperature oxidation resistance so that the abnormal oxidation is unlikely to occur. Moreover, the stainless steel has excellent durability to cooling and heating testing cycles and has a sufficient high-temperature strength.

From the foregoing, it will be understood that the present invention provides a high-aluminium-containing ferritic stainless steel which has improved high-temperature oxidation resistance and high-temperature strength without increasing the amounts of chromium, aluminium and rare earth elements. The stainless steel of the present invention is hence extensively suitable for high-temperature applications such as a catalyst carrier of a catalytic converter provided as an emission control equipment, heating device and electric heating element.

Claims

1. A ferric stainless steel consisting by weight of less than 0.03 % carbon, less than 1 % silicon, less than 1 % manganese, less than 0.04 % phosphorus, less than 0.03 % sulphur, from 15 % to 25 % chromium, less than 0.03 % nitrogen, from 3 % to 6% aluminium, from 0.1 % to 4 % molybdenum, and from 0.01 % to 0.15 % at least one of rare-earth elements and yttrium.

2. A ferric stainless steel as claimed in claim 1 further comprising from 0.05 % to 1 % at least one of

niobium, vanadium and titanium.

3. Use of a steel as claimed in either preceding claim, in the form of foil in the construction of a catalytic convertor.

4. Use of a steel as claimed in claim 1 or claim 2 in the production of a heating element or heating device.

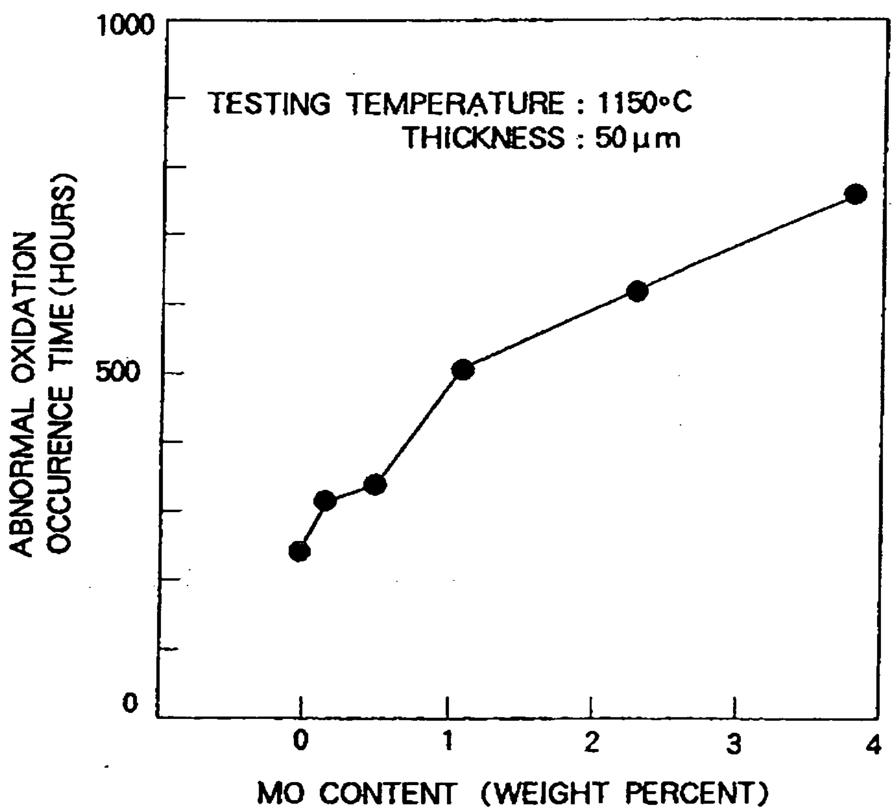
5. Steel as claimed in claim 1 or claim 2 in the form of foil.

6. Steel as claimed in claim 5, in which the foil is fabricated in a honeycomb array.

7. A catalytic convertor for the exhaust system of a motor vehicle which includes steel foil as claimed in claim 5 or claim 6, as catalyst support.

8. A motor vehicle including a catalytic convertor as claimed in claim 7.

FIG.1


TESTING TEMPERATURE : 1150°C
THICKNESS : 50 μm
ABNORMAL OXIDATION OCCURENCE TIME (HOURS)
1000
500
0
0
1
2
3
4
MO CONTENT (WEIGHT PERCENT)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 2329

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	SU-A-552 369 (KOLIADA ET AL.) * the whole document *	1,4	C22C38/22 F01N3/28
X	GB-A-833 446 (AKTIEBOLAGET KANTHAL) * claims 1,4,5,7,9,12 * & DE-B-1 121 099	1,2,4	
A	DE-C-763 358 (HERAEUS-VACUUMSCHMELZE A.G.) * claims 1,6,10 *	1	
A	DE-A-734 854 (HERAEUS-VACUUMSCHMELZE A.G.) * claims 1,5 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C22C
F01N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 AUGUST 1992	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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